STUDY OF 5-NO_2-2-FURALDEHYDE DERIVATIVES, IV.* SCHIFF BASES WITH PYRIDINES AND NITROANILINES**

By

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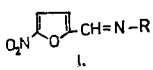
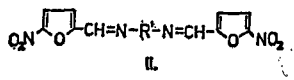
Schiff base derivatives of 5-NO_2-2-furaldehyde with aminopyridines and nitroanilines were prepared, and their u.v. and visible spectra in acidic and basic media are discussed.

In previous papers [1—3] we reported the synthesis and spectral behaviour of several Schiff base derivatives of 5-NO_2-2-furaldehyde (NFA). As a continuation of our investigations on furan derivatives, in the present paper we discuss the u.v. spectral characteristics of the following Schiff bases:



I.



II.

The preparation of the compounds studied and the method of spectral measurements were described previously [1, 3]. The analytical data on our compounds are listed in Table I.

The spectra of the aminopyridine derivatives (Table II) reveal different spectral properties. The spectra of *1* and *3* show two bands, the positions and intensities of which are almost the same in acidic and in alkaline solutions. The spectrum of a neutral methanolic solution of *2* contains two high-intensity bands at 237 and 335 nm, while in acidic and in basic solution three and two bands, respectively, are observed (Fig. 1). The different properties can probably be interpreted by the conjugation extending over the whole molecule; in the case of *2* this is impossible.

Similar observations can be made on the methyl derivatives. The spectra are pH-independent for compounds with 2-CH_3 or 4-CH_3 groups, while those of the 3-CH_3 derivative in neutral alcoholic and in acidic or basic solutions are completely different.

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** Part III.: J. Császár: Acta Phys. et Chem., Szeged, 30, 79 (1984).

Table I

Analytical data on Schiff bases

No.	*R*, *R'* =	M.p.*	C %		H %	
			Calcd.	Found	Calcd.	Found
1		79—81	55.30	55.14	3.25	3.09
2		117—119		54.98		3.16
3		250*		55.20		3.12
4		160—161	53.88	53.58	2.88	2.77
5		146—148	57.14	57.06	3.92	3.79
6		163—165		57.40		3.81
7		200**		57.31		3.78
8		110**	50.71	50.66	2.55	2.48
9		95**		50.58		2.56
10		100**		50.70		2.48
11			50.58	50.59	2.70	2.93
12		144—146		50.59		2.58
13		180**		49.14		2.95

* Uncorrected values; ** decomposed.

The spectral behaviour of Schiff bases with diaminopyridines is interesting. For *8* (Fig. 2) and *10* a very intense colour is formed in acidic or in basic solution, and new bands appear in the visible region; similar changes can not be observed for *9*.

The spectral data on nitroaniline derivatives are listed in Table II. The spectrum of *11* is practically pH-independent. The methanolic solution of *13* shows a high-intensity band at 377 nm; in acidic media there is an inflexion at around 480 nm too. The visible spectrum of a basic solution contains three bands, at 377, 477 and 618 nm (Fig. 3). As the base concentration is varied a set of curves can be recorded, in which the intensities of the 477 and 618 nm bands change in opposite ways; an inflexion point is formed at 480 nm. The change in E_{618} *vs.* base concentration

Table II

U.v. spectral data on Schiff bases of aminopyridines and nitroanilines

No.	nm and log ε data on u.v. bands				
1		235(4.19)	303(4.12)		
		233(3.95)	308(4.05)		
		235(4.15)	309(4.09)		
2		237(4.12)	~275	335(4.21)	
	217(4.48)	233(4.20)	312(4.27)		
		241(4.05)	313(4.01)		
3	205(4.23)	~250	265(4.11)	~300	
	209(4.13)		267(4.12)	~310	
		~247	~270	~315	
4	218(4.30)	~265	310(3.92)		
		265(3.89)	308(4.02)		
		~265	317(3.89)		
5		245(4.06)	325(4.00)*		
		234(4.16)	313(4.29)		
		237(4.20)	303(4.13)		
6		235(4.11)	~290	358(4.26)	
	205(4.28)	236(4.21)	313(4.27)		
		238(4.25)	317(4.19)		
7	203(4.24)	234(4.09)	297(3.91)		
	206(4.35)	~230	300(4.02)		
		236(4.16)	297(3.94)		
8		233(4.01)	310(4.07)		409(3.75)
		~225	312(4.20)		510(3.25)
		~245	313(4.00)		484(3.63)
9		233(3.95)	305(3.83)		~380
	207(4.20)	233(4.20)	307(4.09)		
		~240	310(3.96)		~400
10	208(4.23)	~240	311(4.36)		
		246(4.08)	325(4.20)		
		~230	309(3.58)		~390
11		229(4.33)	296(4.03)	393(3.69)	
		230(4.31)	303(4.08)	406(3.70)	
		230(4.38)	287(4.05)	391(3.69)	
			308(4.03)		
12		232(4.20)	268(4.21)	343(4.27)	
	203(4.46)	251(4.04)		307(4.12)	
		233(4.36)		319(4.14)	
13	~220			377(4.20)	
	~225	~250		362(4.03)	~480
	~230			377(3.86)	477(3.86)
					618(4.01)

* Broad band between 305 and 340 nm.

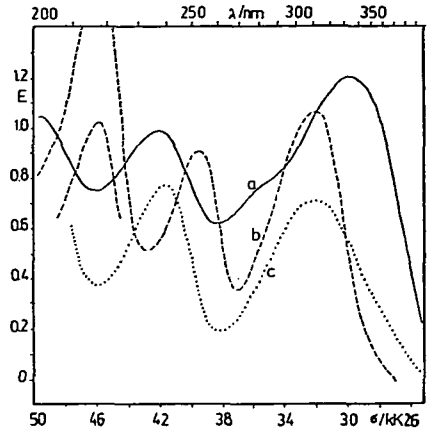


Fig. 1. Spectra of *2*. a: in methanol, $c=7.37\cdot10^{-4}$; b: in 0.1 mol/dm³ H_2SO_4/CH_3OH, $c=8.75\cdot10^{-4}$; c: in 0.1 mol/dm³ $NaOH/CH_3OH$, $c=6.91\cdot10^{-4}$ mol/dm³. $d=0.1$ cm

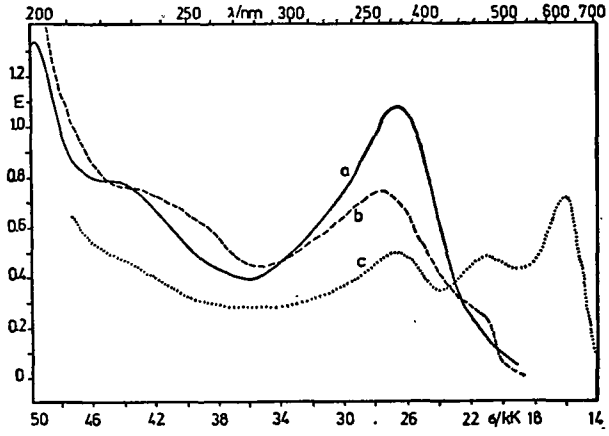
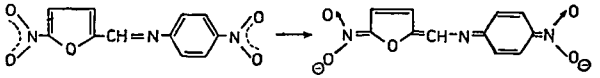


Fig. 2. Spectra of *8*. a: in methanol, $c=7.75\cdot10^{-4}$; b: in 0.1 mol/dm³ H_2SO_4/CH_3OH, $c=6.46\cdot10^{-4}$; c: in 0.1 mol/dm³ $NaOH/CH_3OH$, $c=6.46\cdot10^{-4}$ mol/dm³. $d=0.1$ cm

is shown in Fig. 4. We presume that the above change is due to the participation of NO_2 groups in the conjugation; the strong colour change too can be interpreted in terms of this transformation.



Since the change is reversible, the decomposition of the Schiff bases or the opening of the furan part is not probable.

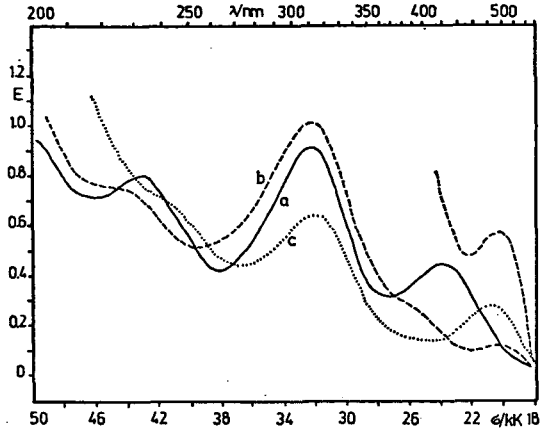


Fig. 3. Spectra of *13*. a: in methanol; b: in 0.1 mol/dm³ H_2SO_4/CH_3OH; c: in 0.1 mol/dm³ $NaOH/CH_3OH$. $c = 6.89 \cdot 10^{-4}$ mol/dm³; $d = 0.1$ cm

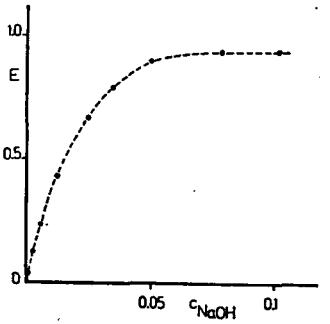


Fig. 4. Plot of the changes in E *vs.* c_{NaOH} for *13*

References

[1] *Császár, J.:* Acta Phys. et Chem. Szeged, **30**, 71 (1984).
[2] *Császár, J., J. Morvay, O. Herczeg:* Acta Phys. et Chem. Szeged, in press.
[3] *Császár, J.:* Acta Phys. et Chem. Szeged, **30**, 79 (1984).

ИССЛЕДОВАНИЕ ПРОИЗВОДНЫХ 5-NO_2-2-ФУРАЛЬДЕГИДА, IV. ОСНОВАНИЯ ШИФФА С ПИРИДИНАМИ И НИТРОАНИЛИНАМИ

Й. Часар

Синтетизированы основания Шиффа, производные 5-NO_2-2-фуральдегида с аминопиридинами и нитроанилинами и рассмотрены их УФ-ые и видимые спектры в кислой и щелочной средах.